Organic/Water Phase Equilibria at High Temperature

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Liquid water between 200 and 300°C is an environmentally benign alternative to traditional hazardous organic solvents. As the temperature is increased from 25 to 250°C, the dielectric constant of water decreases from 80 to 20. With this intermediate dielectric constant, similar to that of acetone, water is able to dissolve organics as well as salts, and these solubilities can be tuned with temperature. Moreover, the dissociation constant of water to H+ and OH- ions is orders of magnitude greater than that in ambient water, facilitating acid- and base-catalyzed reactions. Thus water is an attractive solvent for homogeneous aqueous/organic reactions. The organic reactants are solubilized in the high temperature water. When the reaction is complete, the product mixture is cooled until the desired aqueous/organic phase splitting occurs. The organic products are then recovered by simple decantation, avoiding costly downstream separations such as distillation or crystallization.

Phase equilibria were measured for several organic/water systems with upper critical solution temperatures from 230 to 280°C. Phase boundaries were measured by a traditional cloudpoint technique in a visual, variable volume cell operating temperatures as high as 290°C and 500 bar. Cloudpoints were observed through a sapphire window with a borescope and digital camera. These data were correlated with traditional g^E models.